

Bioenergy residues as soil amendments: climate-relevant C and N dynamics during decomposition

M. L. Cayuela^A, P. J. Kuikman^B, O. Oenema^{A,B}, R. R. Bakker^C and J. W. Groenigen^{A,B}

^ADept. Soil Quality, Wageningen University. PO Box 47, 6700 AA Wageningen, The Netherlands, E-mail marialuz.cayuela@wur.nl

^BAlterra. Wageningen University and Research Centre. PO Box 47, 6700 AA Wageningen, The Netherlands.

^CAgrotechnology & Food Sciences Group. P.O.Box 17, 6700 AA Wageningen, The Netherlands.

Abstract

It is not clear how an expanding bioenergy sector will affect land use and what could be the environmental consequences. Probably the increased bioenergy production will lead to higher input of its by-products to the soil as amendments or fertilizers. However, it is still unclear how these novel by-products of bioenergy production will influence microbial transformation processes in soil, and thereby its greenhouse gas balance and organic matter stocks. In this laboratory incubation study, we compared the greenhouse gas dynamics after application of different bioenergy by-products into an agricultural soil. Ten by-products were selected from different bioenergy sectors: anaerobic digestion (manure digestates), first generation biofuel residues (rapeseed meal, distilled dried grains with solubles), second generation biofuel residues (non-fermentables from hydrolysis of different lignocellulosic materials) and pyrolysis (biochars). These by-products were added at the same N rate (150 kg N/ha) to a moist (80% water filled pore space) sandy soil and incubated at 20 °C for 60 days.

After 60 days, first generation biofuel residues had emitted more than 80% of added C as CO₂. Around 60% was emitted in the case of second generation biofuel residues and 40% with digestates. Biochars were the most stable residues with the lowest CO₂ loss (between 0.5 and 5.8 % of total added C). Regarding N₂O emissions, addition of first generation biofuel residues led to the highest total N₂O emissions (between 2.5 – 6.0% of added N). Second generation biofuel residues emitted between 1.0-2.0% of added N, whereas anaerobic digestates led to emissions lower than 1% of added N. The two biochars used in this study led to negative N₂O emissions, i.e. lower than N₂O emitted from the blank soil. We conclude that, at least in the short term, the effects of biofuel residues on the combined greenhouse gas balance of the soil ranges from beneficial (biochar) via mixed (digestates, second generation biofuels) to manifestly adverse (first generation biofuels). These effects are relevant and should be taken into account in life cycle analyses of biofuel production and assessment of the environmental impact of biofuels and bioenergy.

Key Words

Biofuels by-products, nitrous oxide, carbon dioxide, soil amendments, mineralization.

Introduction

In spite of the large number of studies analysing the benefits of biofuels on the greenhouse gas balance, only a few studies take into account the contribution of residues from biofuel production. Farrell *et al* (2006) underlined the importance of considering the fate of by-products on net energy and GHG calculations. They considered that by-products of ethanol production have a positive economic value and displace competing products that require energy to make. However, large amounts of residues could represent a serious environmental problem leading to elevated GHG emissions if inappropriate management options are selected. The physico-chemical characteristics of the different bioenergy residues vary widely depending on the original biomass and the method used for energy production. But generally speaking, these materials still have a high concentration of C (usually the most recalcitrant fractions). Moreover, they contain a wide range of nutrients that must be recycled in an environmental benign way. It is likely that the intensification of bioenergy production will lead to an increased use and higher input of these by-products to the soil as amendments or fertilizers.

To our knowledge there is a limited number of studies that measure greenhouse gas relevant dynamics such as C mineralization and N₂O emissions after application of bioenergy residues to soil (Moller and Stinner 2009; Spokas *et al.* 2009), and most of them are focused on biogas residues or biochar. No literature is available comparing the main different bioenergy chains and evaluating how the application of N-enriched bioenergy residues will influence microbial transformations processes in soil and thereby the emissions of

greenhouse gases. The aim of this paper is therefore to compare C and N climate relevant gases emissions during decomposition in soil of residues generated by different bioenergy sectors.

Methods

Soil and residues used in the incubation experiment

A sandy agricultural soil (Typic Endoaquoll with 75% sand, 23% silt, 2% clay) (USDA, 1999) was selected for the incubation experiments and sampled from the 10-30 cm layer at the experimental farm "Droevendaal", outside Wageningen, the Netherlands (51°59'N, 5°39'E). Air-dried soil was sieved (< 2 mm) and stored (15 °C) until the beginning of the experiment. Ten organic residues from bioenergy production were selected: residues from anaerobic digestion (cow manure digestate (CMD) and pig slurry digestate (PSD)); first generation biofuel residues (rapeseed meal (RSM) from biodiesel production, dried distillers grains with solubles (DDGS), and two different yeast concentrates (YC1 and YC2) from bioethanol production); second generation biofuel residues (non-fermentables from enzymatic hydrolysis of potato peels (NFPP) and non-fermentables from enzymatic hydrolysis of wheat straw (NFWS); commercially available green waste biochar (GBC) and poultry manure biochar (PBC), both produced by continuous slow pyrolysis at 550 °C. The residues were freeze-dried (except the biochars), ground and sieved (< 0.5 mm) before application to avoid a moisture or particle size effect. Their chemical characteristics are shown in Table 1.

Soil incubations

The incubation experiment was carried out with 500 g (based on oven-dry weight) soil in 1 L glass jars at 20 °C. Before the start of the incubation, the soil was adjusted to ca. 60 % of water holding capacity (WHC) and pre-incubated at 20 °C for 7 days. Subsequently the different organic residues were thoroughly mixed and water was added to adjust moisture to 80% of water filled pore space. The jars were covered by a woven black polyethylene cover, to allow gaseous exchange, but retard evaporation. The incubation jars were maintained in a climatic room with a constant temperature (20 °C) and air humidity (40%). The soil moisture was gravimetrically adjusted 2 times a week with de-ionized water for each individual jar. During the incubation experiment we evaluated CO₂ and N₂O emissions when the different bioenergy residues were applied. The experiment, consisting of 11 treatments: a control (unfertilized soil) and ten bioenergy by-products, was laid out as a randomized block design with five replicates per treatment and lasted 60 days. All the residues were applied at a rate of 150 kg N/ha, corresponding to 50 mg N/kg soil based on a plough layer of 25 cm.

Table 1. Main chemical properties of the bioenergy by-products used in the experiment.

<i>Residue type</i>	<i>Residue</i>	<i>TOC (%)</i>	<i>TN (%)</i>	<i>TOC/TN</i>	<i>pH</i>	<i>EC (dS/m)</i>	<i>WSC (g/kg)</i>	<i>WSN (g/kg)</i>	<i>NH₄⁺ (mg/kg)</i>	<i>NO₃⁻ + NO₂⁻ (mg/kg)</i>
Anaerobic digestion	CMD	41.7	3.2	13.2	9.03	16.80	48.8	4.3	166	4.2
	PSD	37.9	4.4	8.7	8.52	19.77	38.7	11.6	5361	2.5
First generation biofuels	RSM	45.9	6.0	7.7	6.15	2.54	74.4	2.4	180	13.4
	DDGS	48.4	5.4	8.9	5.02	5.40	111.1	4.4	151	2.0
	YC1	48.5	6.2	7.8	4.22	8.36	202.5	12.8	1153	1.9
	YC2	47.4	4.7	10.0	4.05	8.39	220.0	8.7	274	1.5
Second generation biofuels	NFWS	44.8	1.3	34.2	5.82	3.50	135.3	2.0	196	18.0
	NFPP	46.5	3.6	12.9	5.59	2.75	44.3	2.8	292	38.2
Pyrolysis	GBC	86.3	0.3	345	6.55	0.12	0.1	0.0	17	0.4
	PBC	37.0	1.2	29.8	10.25	10.32	0.5	0.0	2	1.8

Measurements of N₂O and CO₂ emissions

Fluxes of N₂O and CO₂ were measured 26 times over a period of 60 days. Gas fluxes were analysed daily during the first six days, decreasing the sampling frequency to four times, three and twice a week subsequently. Changes in the concentration of N₂O in the headspace of the jars after closing the lid were determined with a photo-acoustic infrared analyser (Innova air Tech Instruments, Ballerup, Denmark) which was directly attached to the jars by two Teflon tubes and needles through septa. The gas analyser was fitted with optical filters to measure selectively concentrations of N₂O, CO₂ and water vapour. To prevent a strong accumulation of CO₂ in the headspace of the jars, which may interfere with the N₂O measurements, a soda lime trap was installed in the tube at the inlet to the gas monitor (Velthof *et al.* 2003). CO₂ emissions were measured following a similar setup, but without the soda lime filter and after a separate closing period. The concentration of N₂O and CO₂ were measured 30 min after closing the jar.

Statistical analysis

The impact of the different characteristics of biofuel residues on CO₂ and N₂O losses was determined by redundancy analysis (RDA) using Canoco 4.5 for windows software package. Significance of the ordination axes was calculated by the Monte-Carlo permutation test.

Results and discussion

Application of the bioenergy by-products to the soil resulted in an immediate increase of soil respiration. The highest CO₂ and N₂O fluxes were produced during the first week of incubation. Biochars were the exception with very low respiration rates through the whole incubation period. In the case of green-biochar, respiration was never significantly different than that of the control soil (data not shown). The relative amounts of total C evolved as CO₂ after 60 days differed significantly among residue categories and decreased in the order: first generation biofuel by-products > second generation biofuel by-products > manure digestates > biochars (Table 2). First generation biofuel residues resulted in almost complete decomposition during the experiment, contributing little or nothing to soil organic matter stocks. Conversely, second generation biofuel residues led to a buildup of C comparable to anaerobic digestates. Finally, biochars were by far the most recalcitrant residues, showing therefore the highest C sequestration potential. N₂O emissions followed a similar pattern, with highest losses for first generation biofuel residues. Biochars led to negative (although not statistically significant) N₂O emissions.

Table 2. Percentages of CO₂-C and N₂O-N emitted respect to C and N added with biofuel by-products in soil and total C remaining after 60 days incubation.

Residue type	Residue	CO ₂ -C emitted respect to added C (%)	N ₂ O-N emitted respect to added N (%)	C remaining in soil (g C/kg soil)
Anaerobic digestion	CMD	38 ± 9	0.2 ± 0.1	0.41 ± 0.06
	PSD	42 ± 5	0.8 ± 0.1	0.25 ± 0.02
First generation biofuels	RSM	94 ± 11	5.0 ± 1.3	0.02 ± 0.04
	DDGS	91 ± 12	2.5 ± 0.7	0.04 ± 0.05
	YC1	107 ± 16	6.0 ± 2.7	-0.03 ± 0.06
	YC2	81 ± 12	2.9 ± 0.6	0.10 ± 0.06
Second generation biofuels	NFWS	62 ± 5	1.1 ± 0.3	0.65 ± 0.09
	NFPP	75 ± 13	1.9 ± 0.4	0.16 ± 0.09
Pyrolysis	GBC	0.5 ± 0.2	-0.10 ± 0.03	17.17 ± 0.04
	PBC	6 ± 2	-0.06 ± 0.05	1.40 ± 0.03

Mean ± std error (n=5)

Figure 1 shows the redundancy analysis (RDA) ordination plot. The results of RDA indicated that 96.3 % of the total variance within the investigated parameters was explained by the first and second ordination axis with the different characteristics of the residues as environmental variables. High species-environment correlation (0.984, P=0.002) revealed a strong relation between greenhouse gas emissions and residues characteristics. Total concentration of N in the residue seems to be the most critical factor, highly correlated with both CO₂ and N₂O emissions. Samples from different bioenergy chains clearly grouped with respect to the first ordination axis (x axis), showing their different behaviour with respect to N₂O and CO₂ emissions. The biochars (GBC and PBC) were the residues positioned at the right of the diagram indicating the lowest C and N losses and highest C sequestration potential. Digestates (PSD, CMD) exhibited lower than average emissions, followed by second-generation biofuels (NFPP, NFWS) which were positioned just in the middle. First generation biofuel by-products (RSM, DDGS, YC1, YC2) produced the most adverse impact (high emissions, low C sequestration) and all of them showed higher than average emission values.

Conclusion

With this study we highlight the importance of considering the by-products of bioenergy production on net greenhouse gas balance calculations. Biofuel by-products vary enormously in chemical composition and, when used directly as soil-amendments, they lead to very different climate relevant dynamics. Whereas some may lead to elevated N₂O emissions and contribute little to soil organic matter, others may increase soil organic matter stocks with little N₂O emission. These dynamics need to be taken into account in life-cycle analyses in the future in order to reach a truly integrated assessment of the climate impact of biofuel production.

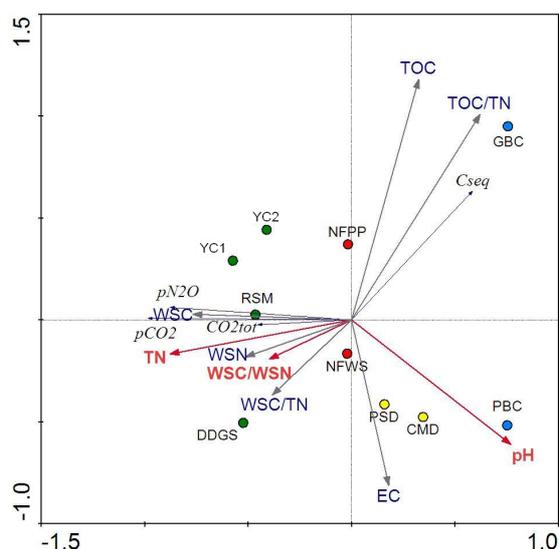


Figure 1. Redundancy analysis (RDA) ordination diagram depicting the residues characteristics responsible for differences in CO₂ and N₂O emissions among the biofuel by-products. The length of the arrows indicates the significance for sample differentiation. Arrows point in the direction of by-products with above average signal. Color legend: green represents first generation biofuel residues, red for second generation residues, yellow for digestates and blue for biochars. pCO₂ and pN₂O represent the percentages of C and N emitted as CO₂ and N₂O respectively. Cseq refers to amount of C remaining in soil after 60 days. For biofuel residues abbreviations see the methods section.

Acknowledgements

The authors thank to Duijnie (Cosun Corporate, The Netherlands) for supplying the first generation biofuel residues, BEST Energies Australia for the supply of biochars and the experimental farm De Marke and Sterksel Pig Research Centre (Animal Science Group, Wageningen University) for the manure digestates. The authors are very grateful to Dr. R de Goede for his kind help with multivariate statistical analysis. This research was supported through a European Community Marie Curie Fellowship.

References

- Farrell AE, Plevin RJ, Turner BT, Jones AD, O'Hare M, Kammen DM (2006) Ethanol can contribute to energy and environmental goals. *Science* **311**, 506-508.
- Moller K, Stinner W (2009) Effects of different manuring systems with and without biogas digestion on soil mineral nitrogen content and on gaseous nitrogen losses (ammonia, nitrous oxides). *European Journal of Agronomy* **30**, 1-16.
- Spokas KA, Koskinen WC, Baker JM, Reicosky DC (2009) Impacts of woodchip biochar additions on greenhouse gas production and sorption/degradation of two herbicides in a Minnesota soil. *Chemosphere* **77**, 571-581.
- Velthof GL, Kuikman PJ, Oenema O (2003) Nitrous oxide emissions from animal manures applied to soil under controlled conditions. *Biology and Fertility of Soil* **37**, 221-230.